



# **$^{18}\text{O}$ in Atmospheric $\text{CO}_2$ Simulated by a 3-D Transport Model: A Sensitivity Study to Vegetation and Soil Fractionation Factors**

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Received 28 October 1996; accepted 8 January 1997

**Abstract.** The  $^{18}\text{O}/^{16}\text{O}$  ratio in atmospheric  $\text{CO}_2$  is a signal dominated by the processes by which the global land biosphere absorbs and respire  $\text{CO}_2$ . Potentially it makes it possible to separate the photosynthesis from the total ecosystem respiration provided that leaf  $\text{CO}_2$  and soil  $\text{CO}_2$  have different isotopic signatures, that the air-sea exchange is correctly treated and that the isotopic value of anthropogenic emissions is well characterized. In this paper we simulate the  $\delta^{18}\text{O}$  of atmospheric  $\text{CO}_2$ , using the 3-D tracer model TM2. We perform a specific sensitivity study of  $\delta^{18}\text{O}$  to the fractionation factors for the diffusion of  $\text{CO}_2$  out of the soils ( $\epsilon_{soil}$ ) and into/out of the leaves ( $\epsilon_{leaf}$ ). The control run is similar to Ciais et al. (1996a). The latitudinal gradient, the seasonal amplitude in the northern hemisphere and the mean long term trend appear to be fairly sensitive to these two factors. The trend is nevertheless the most sensitive but it also highly depend on the atmospheric  $\delta^{18}\text{O}$  mean value and on the stratospheric enrichment of  $^{18}\text{O}$  in  $\text{CO}_2$  pertaining to the photolysis of  $\text{O}_3$ .

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## 1 Introduction

An increasing attention has been given to the isotopes of  $\text{CO}_2$  ( $^{13}\text{CO}_2$  and more recently  $\text{C}^{18}\text{O}^{16}\text{O}$ ), as they bring additional constraints to the global carbon cycle. The oxygen isotopic content of atmospheric  $\text{CO}_2$  is primarily driven by interactions between  $\text{CO}_2$  and the reservoirs of liquid water (see Eq. 2 in Table 1 for isotopic equilibrium between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ). Francey and Tans (1987) showed indeed that direct O atom exchange between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapor does not occur in the gas phase. On the other hand, when  $\text{CO}_2$  dissolves in water, an isotopic equilibrium for oxygen atoms takes place. Because the amount of water available is huge compared to the amount of  $\text{CO}_2$ , the  $^{18}\text{O}/^{16}\text{O}$  ratio in  $\text{CO}_2$  is de-

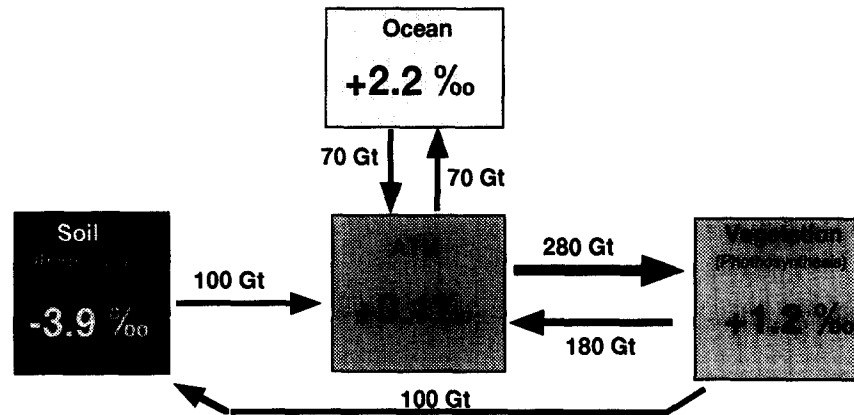
termined by the one of water at a given temperature. Francey and Tans (1987) and Farquhar et al. (1993) pointed out the major influence of  $\text{CO}_2$  exchanges with leaf water (photosynthesis) and soil water (soil respiration). Ciais et al. (1996a,b) further tested these parameterizations in a global 3-D transport model, and obtained reasonable agreement between simulated and observed  $^{18}\text{O}/^{16}\text{O}$  ratio in atmospheric  $\text{CO}_2$ . Following their work, we present here a sensitivity study of this ratio to the fractionation factors involved during the diffusion of  $\text{CO}_2$  out of the soil and into/out of the leaves.

## 2 The observations

$^{18}\text{O}$  in  $\text{CO}_2$  is routinely measured at specific locations around the world from three independent air sampling networks: the NOAA-CU network of 17 sites (Trolier et al., 1996), the SCRIPPS-CIO network of 10 sites (Meijer et al., in preparation), and the CSIRO network of 5-6 sites (Francey et al., 1990). The  $^{18}\text{O}/^{16}\text{O}$  isotopic ratios are reported in the  $\delta$  scale (Eq. 1, Table 1), and  $\delta^{18}\text{O}$  values are expressed in per mil (‰). At a global scale, three major features can be retrieved from the atmospheric observations.

1. A *north minus south difference* of roughly  $-1.5\text{‰}$ : the northern hemisphere is permanently depleted in  $^{18}\text{O}$ , as first observed by Francey and Tans (1987).
2. A strong *seasonal cycle* at high northern latitudes (Keeling, 1961): there is a maximum in early summer and a minimum in early winter. The observed peak-to-peak amplitude is  $1.44\text{‰}$  at Point Barrow ( $71^\circ\text{N}$ ,  $156^\circ\text{W}$ ) while Cape Grim in the southern hemisphere ( $40^\circ\text{S}$ ,  $140^\circ\text{E}$ ) has a lower peak-to-peak amplitude of  $0.4\text{‰}$ .
3. The long time series of the SCRIPPS-CIO network (5 sites since 1977) shows *no long term trend* in the

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**Fig. 1.** The global “pre-anthropogenic” exchange fluxes of CO<sub>2</sub> (in GTC (10<sup>15</sup> g yr<sup>-1</sup>) between the atmosphere and the terrestrial biosphere and the ocean, as well as the isotopic composition of CO<sub>2</sub> (expressed in ‰ PDB-CO<sub>2</sub>), in equilibrium with the exchangeable water. The δ<sup>18</sup>O value of these three reservoirs is weighted in space and time with the exchange fluxes.

mean atmospheric δ<sup>18</sup>O (e.g., record at Mauna-Loa, Meijer *et al.*, private communication).

Exchange with leaves and soils is strongly seasonal over temperate and boreal ecosystems which likely account for most of the observed δ<sup>18</sup>O annual cycle. Moreover the combined effects of photosynthesis and respiration tend to decrease the local δ<sup>18</sup>O in atmospheric CO<sub>2</sub> at high northern latitudes. This pattern follows the composition of precipitation which is depleted in <sup>18</sup>O relative to sea-water towards high latitudes and towards the interior of continents.

### 3 Biospheric fluxes

We coupled the surface exchange fluxes of CO<sub>2</sub> and C<sup>18</sup>O<sup>16</sup>O for each reservoir to an atmospheric 3-D tracer model (TM2) in order to simulate the global distribution of δ<sup>18</sup>O in atmospheric CO<sub>2</sub>. The TM2 model (Heimann, 1995) uses atmospheric forcing from ECMWF in Reading (UK) and it is run at a resolution of 7.5° by 7.5° in the horizontal, with 9 vertical levels ( $\sigma$  coordinates). We will focus on the global “pre-anthropogenic” steady state budget of δ<sup>18</sup>O in atmospheric CO<sub>2</sub> and more specifically on the terrestrial biospheric fluxes. Figure 1 presents the CO<sub>2</sub> gross exchange fluxes between the atmosphere and the vegetation, the soils and the ocean, as well as the δ<sup>18</sup>O of CO<sub>2</sub> in isotopic equilibrium with chloroplast water, soil water or sea surface water. The main equations used to describe these processes are reported in Table 1.

– *Leaf exchange* : During photosynthesis, all of the atmospheric CO<sub>2</sub> that enters the chloroplasts, isotopically equilibrates with the evaporating water, in presence of enzyme Carbonic Anhydrase. Some of the CO<sub>2</sub> is then assimilated by photosynthesis

(net Assimilation, A) but more than half of it diffuses back to the atmosphere. Chloroplast water is enriched in <sup>18</sup>O compared to soil water because heavier water molecules evaporate less efficiently than the lighter ones. The degree of enrichment of leaf water is sensitive to the relative humidity, the canopy temperature and to <sup>18</sup>O/<sup>16</sup>O ratio in water vapor (Craig and Gordon, 1965). It can be thus highly variable in space and time: the Assimilation weighted mean value in our simulation is +1.2‰ (Fig. 1). Moreover C<sup>18</sup>O<sup>16</sup>O diffuses more slowly than C<sup>16</sup>O<sub>2</sub> into/out of the leaves (coefficient  $\alpha_1$  in equation 3, Table 1). The overall effect of photosynthesis is to increase the δ<sup>18</sup>O in atmospheric CO<sub>2</sub>.

– *Soil exchange* : The decomposition of dead organic matter by soil microorganisms and root respiration in the soil produce CO<sub>2</sub> which diffuses up to the atmosphere. This net flux augmented by the stem and twigs respiration, balances on annual mean the net uptake of CO<sub>2</sub> during photosynthesis. We thus neglect any net carbon storage or loss by ecosystems on an annual mean basis. Diffusion in the soil is likely slow enough for CO<sub>2</sub> to fully exchange <sup>18</sup>O with the water at the soil surface, even without Carbonic Anhydrase (Ciais *et al.*, 1996a). The <sup>18</sup>O/<sup>16</sup>O ratio of soil water tends to follow the variations in surface soil moisture, and thereof the precipitation. This leads in our simulation to a respiration weighted mean value of -3.9‰ for CO<sub>2</sub> isotopically equilibrated with soil water (Fig. 1). As for leaf exchange, a diffusive fractionation occurs during diffusion of CO<sub>2</sub> out of the soil (coefficient  $\alpha_s$  in equation 4, Table 1), and the effect of soil respiration is to decrease the δ<sup>18</sup>O in atmospheric CO<sub>2</sub>.

- *Ocean exchange* : The net  $\text{CO}_2$  flux between the ocean and the atmosphere can be split in two gross (one way) fluxes (equation 5, Table 1). The  $\text{CO}_2$  gross flux out of the ocean is assumed to be isotopically equilibrated with sea-water, according to reaction (2). The  $\delta^{18}\text{O}$  of sea-surface water is computed from the sea-surface temperature and the salinity, as in Farquhar et al. (1993). The fractionation during  $\text{CO}_2$  diffusion at the air-sea interface is very small ( $-0.8\text{‰}$ ) and the global effect of air-sea exchange is to increase the atmospheric  $\delta^{18}\text{O}$  value (Fig. 1).
- *Stratospheric enrichment* : Recent measurements of  $\delta^{18}\text{O}$  of  $\text{CO}_2$  reported by Gamo et al. (1989) showed a mass independent enrichment in  $^{18}\text{O}$  of  $2\text{‰}$  in the lower stratosphere (19 km) relative to the mean tropospheric value. This enrichment increases with altitude and pertains to the photolysis of  $\text{O}_3$  in the stratosphere (Yung et al., 1991). We parameterized this effect by simply adding a source of  $\text{C}^{18}\text{O}^{16}\text{O}$ , constant in time and space in the upper two levels of the transport model in order to simulate a mean vertical profile of  $\delta^{18}\text{O}$  of  $\text{CO}_2$  close to that observed (Fig. 4).

The  $\text{CO}_2$  gross fluxes between the atmosphere and the vegetation ( $F_{la}$  and  $F_{al}$ , Table 1) are derived from the SIB2 land-surface parameterization (Sellers et al., 1986, 1996; Randall et al., 1996) coupled to the CSU-GCM (Randall et al., 1992; Randall and Pan, 1993; Fowler et al., 1996). The total respiration ( $F_{resp}$ , Table 1) equals the net assimilation of carbon over a year but it is distributed in time according to the ground moisture and soil temperature. The oceanic gross fluxes ( $F_{oa}$  and  $F_{ao}$ , Table 1) are calculated using  $\Delta p\text{CO}_2$  from the Hamburg Model of the oceanic carbon cycle (Maier-Reimer, 1993; Six and Maier-Reimer, 1996), and gas exchange coefficients derived from ECMWF 10 meter wind fields. These coefficients follow the Liss and Merlivat relationship (Liss and Merlivat, 1986) and they are scaled by a global factor of 1.9 in order to be consistent with the global inventory of  $^{14}\text{C}$  in the ocean. The monthly means  $\delta^{18}\text{O}$  of precipitation are taken from the GISS simulations (Jouzel et al., 1987). We run the tracer model for each component described above and with the atmospheric wind fields corresponding to the period 1990-1994. The choice of this particular period has no importance regarding the mean budget of  $\delta^{18}\text{O}$  in  $\text{CO}_2$ . The specific  $\delta^{18}\text{O}$  field relative to one process can be then calculated. But as the  $\delta$  fields are not additive we use the  $\delta$ -anomalies ( $\delta^*$ , defined in Eq. 1, Table 1) which are additive, in order to combine and compare several components (Fig. 2-3).

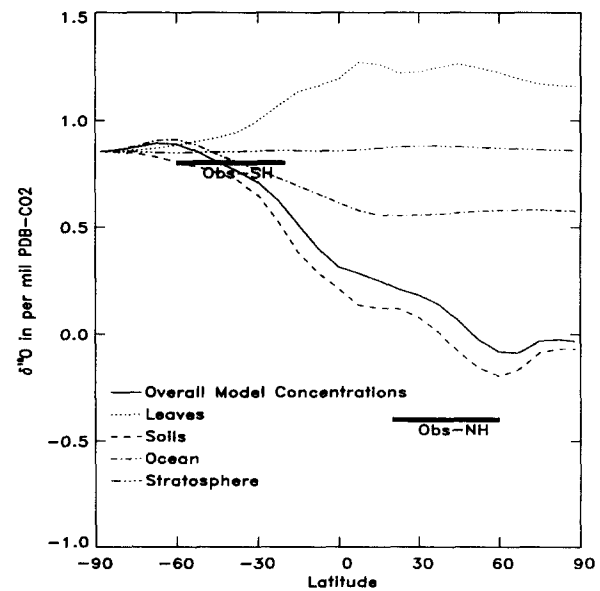


Fig. 2. Simulated  $\delta^{18}\text{O}$ -anomalies ( $\delta^*$ , see equation 1, Table 1) of atmospheric  $\text{CO}_2$  at the surface using the 3-D transport model TM2 (zonal average). The different components correspond to the separate  $\delta^{18}\text{O}$  implied by leaf exchange, soil exchange, ocean exchange and stratospheric enrichment. The observations represent the mean value between  $20^\circ$  and  $60^\circ$  for the northern hemisphere and between  $20^\circ$  and  $60^\circ$  for the southern one (derived from a zonal fit to the observations made by the NOAA-CU network).

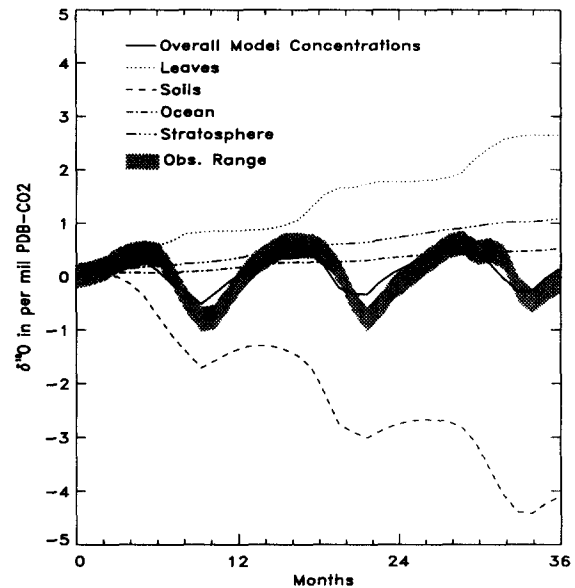


Fig. 3. Simulated  $\delta^{18}\text{O}$ -anomalies ( $\delta^*$ ) in atmospheric  $\text{CO}_2$  simulated at Point Barrow ( $71^\circ\text{N}$ ,  $156^\circ\text{W}$ ) for the period 1990 to 1993. The different components are as in Fig. 2. The grey region represent the observations from the NOAA-CU network (the range is two times the standard deviation of the function used to fit the observations).

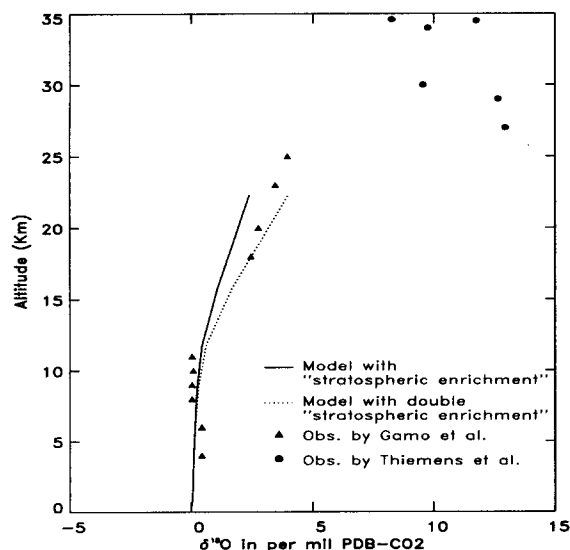


Fig. 4. Simulated  $\delta^{18}\text{O}$ -anomalies ( $\delta^*$ ) in atmospheric  $\text{CO}_2$  averaged over all grid points (vertical profile). The dot curve corresponds to a simulation where the "stratospheric enrichment" is double compared to the control run (solid line). Triangles are data by Gamo *et al.* (1989) over Japan and circles by Thiemens and Jackson (1991) over Palestine.

#### 4 Sensitivity of $\delta^{18}\text{O}$ in $\text{CO}_2$ to fractionation factors

##### 4.1 Control run

Ciais *et al.* (1996b) realized a simulation of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  over the course of a year. Their results fit reasonably well the observations in terms of north minus south difference and seasonal amplitudes at the Point Barrow, Mauna-Loa and Cape Grim stations. We use in this study a slightly different control run. The  $\text{CO}_2$  exchange coefficient for the oceanic fluxes ( $K_{ex}$  in equation 5, Table 1) is derived from Liss and Merlivat relationship instead of from the stability dependent theoretical formulation of Erickson (1993). We also included the stratospheric enrichment of  $^{18}\text{O}$  in  $\text{CO}_2$ , for the "pre-industrial" scenario.

Figure 2 plots the zonal average of the simulated  $\delta^{18}\text{O}$ -anomalies ( $\delta^*$ ) at the surface. It shows the relative contribution of the terrestrial biosphere and of the ocean and the opposite effect of vegetation and soils. The simulated north-south gradient is compared to an estimate of the observed difference between the northern and the southern hemisphere (see caption, Fig. 2). This control run with only the "pre-industrial" fluxes explain a large part of the observed difference, although the additional depletion of the  $^{18}\text{O}/^{16}\text{O}$  ratio in  $\text{CO}_2$  due to fossil fuel burning is missing in this scenario.

Figure 3 presents the simulated trend in  $\delta^{18}\text{O}$ -anomalies ( $\delta^*$ ) at Point Barrow ( $71^\circ\text{N}$ ,  $156^\circ\text{W}$ ) for each compo-

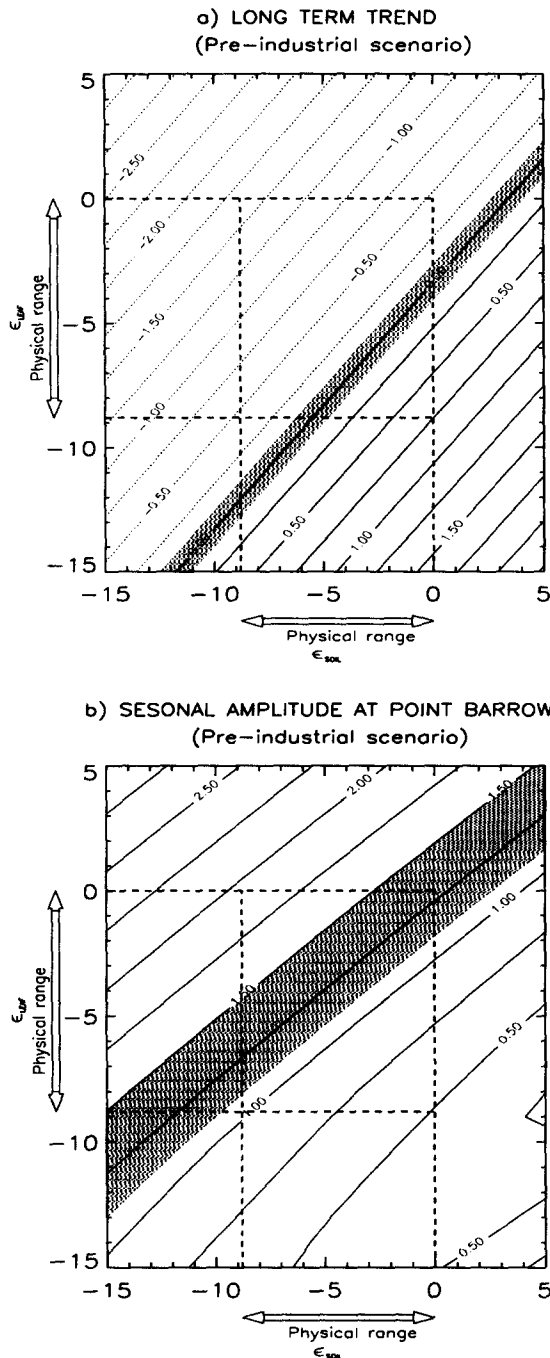
nents as well as the observations from the NOAA-CU network. The trend is primarily determined by the biospheric exchanges, while the ocean plays a weaker role. There is a competing effect between soils and vegetation for the net budget of  $^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . While the ecosystem global respiration depletes the atmospheric  $\text{CO}_2$  in  $^{18}\text{O}$ , the photosynthesis enriches it. Ciais *et al.* (1996b) used only a global formulation similar to equation 6 (Table 1). They solved this global equation for the parameter  $\alpha_s$  to obtain a zero trend for  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . In our simulation, we verified that with the TM2 model such an approach gives similar results if we compare the real trend simulated at many locations and the one calculated through the global budget.

Concerning the "pre-anthropogenic" steady state budget for  $^{18}\text{O}$  in  $\text{CO}_2$  we would like to simulate a long term trend close to zero as well as realistic inter-hemispheric difference and seasonal amplitude at Point Barrow. Even if the exchange time for the oxygen atom in  $\text{CO}_2$  with the biosphere was estimated by Farquhar *et al.* (1993) to be much smaller than with the ocean (2.2 and 8.3 years respectively), the two reservoirs are connected to each other by the mean atmospheric  $\delta^{18}\text{O}$  level. At long time-scales both reservoirs will thus contribute to the mean  $\delta^{18}\text{O}$  value. Concerning the biosphere, the  $\delta^{18}\text{O}$  fluxes (Eqs. 3-4, Table 1) are driven mainly by the  $\text{CO}_2$  gross exchanges fluxes ( $F_{resp}$ ,  $F_{al}$ ,  $F_{la}$ ), the isotopic ratio of water in isotopic equilibrium with  $\text{CO}_2$  and the fractionation during the diffusion of  $\text{CO}_2$  ( $\alpha_s$  and  $\alpha_l$ ). In the following, we specifically analyze the sensitivity of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  to the two fractionation factors.

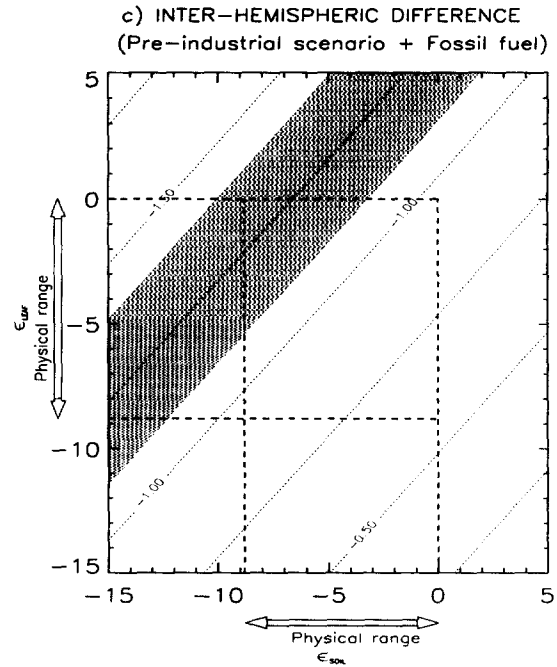
##### 4.2 Sensitivity to the fractionation factors $\epsilon_s$ and $\epsilon_l$

Figure 5 presents the results of three sensitivity tests where the two fractionation factors  $\epsilon_s = (\alpha_s - 1) \cdot 10^3$  and  $\epsilon_l = (\alpha_l - 1) \cdot 10^3$  vary over a given physical range (the other parameters were set as in the control run). These tests were performed with only one simulation. We multiplied the concentration fields produced by the transport model (TM2) with the desired  $\epsilon_s$  and  $\epsilon_l$  coefficients. This is possible because these coefficients only scale the  $^{18}\text{O}$  fluxes (Eqs. 3-4, Table 1) and because the concentration fields produced by TM2 for each component are additive. The first plot (Fig. 5a) presents the  $\delta^{18}\text{O}$  trend in atmospheric  $\text{CO}_2$  at Point Barrow. Because of the relatively short mixing time for  $\text{CO}_2$  in the atmosphere, the trend at this station represents well the mean atmospheric trend, when sources and transport are at steady state. We realized the same sensitivity test for the seasonal amplitude at Point Barrow (Fig. 5b) and for the global difference between the northern hemisphere and the southern hemisphere (Fig. 5c: difference calculated as in Fig. 2). In grey we shade the region that corresponds to realistic "observed" values for the three quantities. We made the assumption that

a steady state was reached at “pre-industrial” time with a long term trend close to zero and that the amplitude of the seasonal cycles has not significantly changed compared to the actual observations.



Concerning the inter-hemispheric difference (Fig. 5c) the contribution of the burning of fossil fuel is to increase by 0.3 ‰ this difference (e.g., Ciais et al. (1996b)). In this case we thus added this component to the “pre-



**Fig. 5.** Sensitivity test of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  simulated by TM2, to the fractionation factor involved during  $\text{CO}_2$  diffusion out of soils ( $\epsilon_{\text{soil}}$ ) and  $\text{CO}_2$  diffusion into/out of the leaves ( $\epsilon_{\text{leaf}}$ ). (a) correspond to the long term trend, (b) to the seasonal amplitude at Point Barrow (71°N, 156°W), and (c) to the inter-hemispheric difference (we took grid points between 20° and 60° for the northern hemisphere and between 20° and 60° for the southern one). (a) and (b) result only from the biospheric fluxes (“pre-industrial” scenario) while (c) includes also fossil fuel burning. The grey regions correspond to the observed range of values for each case.

industrial” budget in order to compare simulated differences in a realistic way to values given by the actual observations. We can also notice that fossil fuel should have induced a negative trend in the atmosphere of -0.14 ‰ per year. As this decrease is not observed in the measurements, other mechanisms must compensate for this effect in today’s  $\delta^{18}\text{O}$  budget as opposed to the “pre-industrial” simulation.

In each of these plots, we defined a physical range for the fractionation factors. The lower limit (-8.8 ‰) corresponds to molecular diffusion with slower diffusion of  $\text{C}^{18}\text{O}^{16}\text{O}$  compared to  $\text{C}^{16}\text{O}_2$ . On the other hand a value of zero would reflect no diffusive discrimination against  $^{18}\text{O}$ . For soils this extreme value seems unrealistic but the closer the  $\text{CO}_2$  production to the soil surface is, the weaker the influence of the diffusive fractionation would be because of competition between the isotopic exchange of  $\text{CO}_2$  with water and the diffusion of  $\text{CO}_2$  out of the soil (Hesterberg and Siegenthaler, 1991).

The main feature that comes out of these graphs is a large sensitivity of the three quantities to the fractionation factors. Nevertheless the long term trend presents

the largest sensitivity within the physical range defined for  $\epsilon_s$  and  $\epsilon_l$ , compared to the seasonal amplitude and the north minus south difference. We also notice that for the trend and the north minus south difference, the iso-lines follow the diagonal which indicates a linear response to both fractionation factors. On the other hand, the seasonal amplitude is more sensitive to  $\epsilon_l$  than to  $\epsilon_s$  (the slope of the iso-lines is smaller).

#### 4.3 Discussion

By changing the two fractionation factors we can find a set of values that would give a reasonable agreement with the observations for both the amplitude and the inter-hemispheric difference. Concerning the long term trend, a different set of values would be required. Nevertheless this latter constraint also highly depends on other parameters. It is first sensitive to the mean  $\delta^{18}\text{O}$  value of atmospheric  $\text{CO}_2$  ( $\delta_a$  in equations in Table 1). A change of +1‰ in  $\delta_a$  for the calculation of the  $\text{C}^{18}\text{O}^{16}\text{O}$  flux associated with the photosynthesis ( $^{18}F_{leaves}$  in Eq. 3, Table 1) would induce a change of +0.4‰ per year in the mean long term trend. Globally the measurements of  $\delta_a$  remain relatively sparse in term of spatial coverage and associated uncertainties are large, particularly over the tropics due to possible reaction between  $\text{CO}_2$  and water in the flask samples. The trend also depends on the “stratospheric enrichment” of  $^{18}\text{O}$  in  $\text{CO}_2$  through isotopic exchange between  $\text{CO}_2$  and  $\text{O}_3$  (e.g., Yung *et al.* (1991)). Figure 4 plots the simulated vertical profile for the control run defined with a given “stratospheric enrichment” (solid line). In this case the isotopic exchange between  $\text{CO}_2$  and  $\text{O}_3$  induces a mean long term trend for  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  of +0.36‰  $\text{yr}^{-1}$  (see Fig. 3). The dot curve in figure 4 shows the same vertical profile for a simulation where we double the “stratospheric enrichment”. The resulting profile is still in agreement with the observations of Gamo *et al.* (1989) and Thiemens and Jackson (1991), and in this case the contribution of the “stratospheric enrichment” to the mean long term trend is twice that in the control run: +0.72‰  $\text{yr}^{-1}$ . It is still difficult to select one profile from the other because (i) the measurements of  $\delta^{18}\text{O}$  in stratospheric  $\text{CO}_2$  are lacking, (ii) the isotopic exchange between  $\text{CO}_2$  and  $\text{O}_3$  is still poorly understood and (iii) we know that the transport model TM2 overestimates vertical mixing between the troposphere and the stratosphere (the tropopause is located at too high altitudes). The range of uncertainty for  $\delta_a$  and for the “stratospheric enrichment” are thus large enough to fulfill the trend constraint with different sets of values within the physical range for the fractionation factors  $\epsilon_s$  and  $\epsilon_l$ . The two other constraints (amplitude and inter-hemispheric difference) could be fulfilled with only one set of values for  $\epsilon_s$  and  $\epsilon_l$ , but this would lead to a fairly low discrimination of  $^{18}\text{O}$  during  $\text{CO}_2$  diffusion through leaves.

**Table 1.** Equations for exchanges of oxygen isotope of  $\text{CO}_2$  with terrestrial ecosystems.

<b>EQUATIONS</b>	
<b>Notation : <math>\delta</math> and <math>\delta</math>-anomalies (<math>\delta^*</math>)</b>	
$\delta_i = \left( \frac{(^{18}\text{O}/^{16}\text{O})_i}{(^{18}\text{O}/^{16}\text{O})_{\text{PDB-CO}_2}} - 1 \right) 10^3$ ;	$\delta_i^* = \frac{C_i(\delta_i - \delta_{bg})}{\sum_i C_i}$ (1)
<b>Isotopic equilibrium with water :</b>	
$\text{COO} + \text{H}_2^{18}\text{O} \rightleftharpoons \text{CO}^{18}\text{O} + \text{H}_2\text{O}$	
with $\alpha_{equ} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{CO}_2}}{(^{18}\text{O}/^{16}\text{O})_{\text{H}_2\text{O}}} = f(T)$ (2)	
<b>LEAF exchange of <math>^{18}\text{O}</math> :</b>	
$^{18}F_{leaves} = -\alpha_l R_a F_{al} + \alpha_l R_l F_{la}$	
with $A = -F_{al} + F_{la}$ (3)	
<b>SOIL exchange of <math>^{18}\text{O}</math> :</b>	
$^{18}F_{soils} = -\alpha_s R_s F_{resp}$ (4)	
<b>OCEAN exchange of <math>^{18}\text{O}</math> :</b>	
$^{18}F_{ocean} = -\alpha_w R_a F_{ao} + \alpha_w R_o F_{oa}$	
with $F_{oa} - F_{ao} = Kex \Delta p\text{CO}_2$ (5)	
<b>Global mass balance (with the <math>\delta</math>-notation) :</b>	
$C_a d\delta_a/dt = A \Delta_a + R_{soils}(\delta_s - \delta_a + \epsilon_s)$	
$+ \epsilon_w(F_{ao} - F_{oa}) + F_{oa}(\delta_o - \delta_a)$ (6)	
<b>SYMBOLS</b>	
A	Net rate of $\text{CO}_2$ assimilation
$F_{resp}$	$\text{CO}_2$ released by soil and plant respiration
$^{18}F_{soils}$	Flux of $\text{C}^{18}\text{O}^{16}\text{O}$ from soils
$^{18}F_{leaves}$	Flux of $\text{C}^{18}\text{O}^{16}\text{O}$ from leaves
$^{18}F_{ocean}$	Flux of $\text{C}^{18}\text{O}^{16}\text{O}$ from ocean
$F_{al}$	Gross flux of $\text{CO}_2$ into the leaves
$F_{la}$	Gross flux of $\text{CO}_2$ out of the leaves
$F_{ao}$	Gross flux of $\text{CO}_2$ into the ocean
$F_{oa}$	Gross flux of $\text{CO}_2$ out of the ocean
$Kex$	exchange coefficient for $\text{CO}_2$ between the atmosphere and sea-surface water
$\Delta p\text{CO}_2$	Difference in partial pressure of $\text{CO}_2$ between the air and sea water
$\alpha_{equ}$	Isotopic equilibration factor between $\text{CO}_2$ and $\text{H}_2\text{O}$
$\alpha_s$	$\text{CO}_2$ fractionation factor for diffusion out of soil
$\alpha_l$	$\text{CO}_2$ fractionation factor for diffusion into/out of the leaves
$\alpha_w$	Fractionation factor for $\text{CO}_2$ during dissolution and diffusion in water
$\epsilon_s, \epsilon_l, \epsilon_w$	$(\alpha_i - 1) \cdot 10^3$ (for $i = s, l, w$ )
$R_s$	$^{18}\text{O}/^{16}\text{O}$ ratio of $\text{CO}_2$ in isotopic equilibrium with soil moisture
$R_l$	$^{18}\text{O}/^{16}\text{O}$ ratio of $\text{CO}_2$ in isotopic equilibrium with chloroplast water
$R_o$	$^{18}\text{O}/^{16}\text{O}$ ratio of $\text{CO}_2$ in isotopic equilibrium with sea-water
$R_a$	$^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric $\text{CO}_2$ : zonal fit (Loess curve) to the monthly mean $\delta^{18}\text{O}$ values derived from the NOAA-CU observations
$\delta_a, \delta_s, \delta_o$	isotopic ratio in $\delta$ units for atmosphere, soil, ocean
$\delta_{bg}$	“background” atmospheric $\delta$ (set up to 0.0‰)
$\delta_i$	simulated $\delta$ field corresponding to process $i$
$\Delta A$	Discrimination against $^{18}\text{O}$ (compared to $^{16}\text{O}$ ) during net $\text{CO}_2$ assimilation by photosynthesis (Farquhar <i>et al.</i> , 1993)
$C_a$	Number of moles of $\text{CO}_2$ in the atmosphere
$C_i$	Concentration field corresponding to process $i$
PDB- $\text{CO}_2$	$\text{CO}_2$ derived from Pee Dee Belemnite calcite

## 5 Conclusion

This short study discusses the sensitivity of the seasonal amplitude, the north minus south difference and the long term trend of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  to the fractionation factors for diffusion of  $\text{CO}_2$  out of the soil and into/out of the leaves. Variation of these factors within the physical range induce large variations of the atmospheric  $\delta^{18}\text{O}$  signal. The long term trend is nevertheless the most sensitive. But the simulation of this quantity highly depends on others processes such as the "stratospheric enrichment" of  $^{18}\text{O}$  in  $\text{CO}_2$  (discussed above) and on the isotopic composition of the water in the leaves. The  $\delta^{18}\text{O}$  of the water inside the chloroplast is fairly sensitive to the  $\delta^{18}\text{O}$  of the water vapor inside the canopy. As a first test we changed the  $\delta^{18}\text{O}$  of water vapor to the extreme case where it is set to the  $^{18}\text{O}/^{16}\text{O}$  ratio of precipitation (i.e., assuming that vapor in the canopy is constituted by 100% of plant transpiration). In this case we obtain a positive long term trend with only little changes of the seasonal amplitude and the latitudinal gradient.

*Acknowledgements.* We would like to thanks the ESCOBA project, PNEDC-France for the financial support of this research.

## References

- Ciais, P., Denning, A. S., Tans, P. P., Berry, J. A., Randall, D. A., Collatz, G. J., Sellers, P. J., White, J. W., Trollier, M., Meijer, H. A. J., Francey, R. J., Monfray, P., and Heimann, M., A three dimensional synthesis study of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ , Part I : Surface fluxes, *J. Geophys. Res.*, *in press*, 1996a.
- Ciais, P., Tans, P. P., Denning, A. S., Francey, R. J., Trollier, M., Meijer, H. J., White, J. W., Berry, J. A., Randall, D. A., Collatz, J. J. G., Sellers, P. J., Monfray, P., and Heimann, M., A three dimensional synthesis study of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ , Part II : Simulations with the TM2 transport model, *J. Geophys. Res.*, *in press*, 1996b.
- Craig, H. and Gordon, A., Deuterium and Oxygen-18 variations in the ocean and the marine atmosphere, in *Stable isotopes in Oceanic Studies and Paleotemperatures*, edited by Laboratory of geology and Nuclear Science, Pisa, 1965.
- Erickson, D. J., A stability dependent theory for air-sea exchange, *J. Geophys. Res.*, *98*, 8471–8488, 1993.
- Farquhar, G. D., Lloyd, J., Taylor, J. A., Flanagan, L. B., Syvertsen, J. P., Hubick, K. T., Wong, S., and Ehleringer, J. R., Vegetation effects on the isotope composition of oxygen in atmospheric  $\text{CO}_2$ , *Nature*, *363*, 439–443, 1993.
- Fowler, L. A., Randall, D. A., and Rutledge, S. A., Liquid and ice cloud microphysics in the CSU General Circulation Model. Part I : Model description and simulated microphysical processes, *J. Climate*, *9*, 489–529, 1996.
- Francey, R. J. and Tans, P., Latitudinal variation in oxygen-18 of atmospheric  $\text{CO}_2$ , *Nature*, *327*, 495–497, 1987.
- Francey, R. J., Robbins, F. J., Allison, C. E., and Richards, N. G., The CSIRO global survey of  $\text{CO}_2$  stable isotopes, in *Baseline Atmospheric Research Program (Australia) 1988*, edited by S. R. Wilson and G. P. Ayers, Department of Administrative Services/Bureau of Meteorology and CSIRO Division of Atmospheric Research, 1990.
- Gamo, T., Tsutsumi, M., Sakai, H., Nakazawa, T., Tanaka, M., Honda, H., and Kubo, H., Carbon and oxygen isotopic ratios of carbon dioxide of a stratospheric profile over Japan, *Tellus*, *41B*, 127–133, 1989.
- Heimann, M., The global atmospheric tracer model TM2 : Model description and user manual, Tech. Rep. 10, Max Planck Institut fur Meteorologie, Hamburg, 1995.
- Hesterberg, R. and Siegenthaler, U., Production and stable isotopic composition of  $\text{CO}_2$  in a soil near Bern, Switzerland, *Tellus*, *43B*, 197–205, 1991.
- Jouzel, J., Russell, G. L., Suozzo, R. J., Koster, R. D., White, J. W. C., and Broecker, W. S., Simulations of the HDO and  $\text{H}_2^{18}\text{O}$  atmospheric cycles using the NASA/GISS general circulation model : The seasonal cycle for present-day conditions, *J. Geophys. Res.*, *92*, 14739–14760, 1987.
- Keeling, C. D., The concentration and isotopic abundance of carbon dioxide in rural and marine air, *Geochimica et Cosmochimica Acta*, *24*, 277–298, 1961.
- Liss, P. S. and Merlivat, L., Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, pp. 113–127, D. Reidel, 1986.
- Maier-Reimer, E., Geochemical cycles in an ocean general circulation model. preindustrial tracer distributions, *Global Biogeochem. Cycl.*, *7*, 645–677, 1993.
- Randall, D. A. and Pan, D. M., Implementation of the Arakawa-Schubert parameterization with a prognostic closure, in *The Representation of Cumulus Convection in Numerical Models*, edited by K. Emanuel and D. Raymond, pp. 137–144, American Meteorological Society, 1993.
- Randall, D. A., Shao, Q., and Moeng, C.-H., A second-order bulk boundary-layer model, *J. Atmos. Sci.*, *49*, 1903–1923, 1992.
- Randall, D. A., Dazlich, D. A., Zhang, C., Denning, A. S., Sellers, P. J., Tucker, C. J., Bounoua, L., Berry, J. A., Collatz, G. J., Field, C. B., Los, S. O., Justice, C. O., and Fung, I., A revised land surface parameterization (SiB2) for atmospheric GCMs. Part III : The greening of the Colorado State University General Circulation Model, *J. Climate*, *9*, 738–763, 1996.
- Sellers, P. J., Mintz, Y., Sud, Y. C., and Dalcher, A., A simple biosphere model (SiB) for use within general circulation models, *J. Atmos. Sci.*, *43*, 505–531, 1986.
- Sellers, P. J., Randall, D. R., Collatz, G. J., Berry, J. A., Field, C. B., Dazlich, D. A., Zhang, C., Collelo, G. D., and Bounoua, L., A revised land surface parameterization (SiB2) for atmospheric GCMs. Part I : Model formulation, *J. Climate*, *9*, 676–705, 1996.
- Six, K. D. and Maier-Reimer, E., Effect of plankton dynamics on seasonal carbon fluxes in an ocean general circulation model, *Global Biogeochem. Cycl.*, *in press*, 1996.
- Thiemens, M. H. and Jackson, T., Oxygen isotope fractionation in stratospheric  $\text{CO}_2$ , *Geophys. Res. Letters*, *18*(4), 669–672, 1991.
- Trolrier, M., White, J., Tans, P., Masarie, K., and Gemery, P., Monitoring the isotopic composition of atmospheric  $\text{CO}_2$  : measurements from the NOAA global air sampling network, *Global Biogeochem. Cycl.*, *accepted*, 1996.
- Yung, Y. L., DeMore, W. B., and Pinto, J. P., Isotopic exchange between carbon dioxide and ozone via  $\text{o}(\text{1d})$  in the stratosphere, *Geophys. Res. Letters*, *18*(1), 13–16, 1991.